

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
25 May 2001 (25.05.2001)

PCT

(10) International Publication Number  
**WO 01/35719 A2**

(51) International Patent Classification: Not classified

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(21) International Application Number: PCT/US00/41774

(84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

(22) International Filing Date:  
2 November 2000 (02.11.2000)

(25) Filing Language: English

Published:  
— Upon request of the applicant, before the expiration of the time limit referred to in Article 21(2)(a).  
— Without international search report and to be republished upon receipt of that report.  
— Without classification; title and abstract not checked by the International Searching Authority.

(26) Publication Language: English

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



**WO 01/35719 A2**

(54) Title: USE OF CARBOXYMETHYL CELLULOSE ACETATE BUTYRATE (CMCAB) IN A WOOD STAIN FORMULATION TO PROVIDE GOOD ADHESION UNDER AN OVERCOAT

(57) Abstract: The invention provides a method for making a stained wood substrate having an overcoat, with improved adhesion of the overcoat. The process comprises the steps of applying an aqueous carboxymethyl cellulose acetate butyrate stain composition to a wood substrate, forming a stained wood substrate. The stained wood substrate is then dried. Next, an overcoat is applied to the stained wood substrate, forming a coated, stained wood substrate. The coated, stained wood substrate is then cured. According to the invention, the aqueous carboxymethyl cellulose acetate butyrate stain composition used in the process comprises carboxymethyl cellulose acetate butyrate, optionally a colorant, water, and an organic solvent.

## USE OF CARBOXYMETHYL CELLULOSE ACETATE BUTYRATE (CMCAB) IN A WOOD STAIN FORMULATION TO PROVIDE GOOD ADHESION UNDER AN OVERCOAT

### BACKGROUND

Cellulose esters are polymers, which are useful in many plastic, film, coating and fiber applications. In coatings applications, cellulose esters are generally applied from organic solvent solutions. However, in an increasing number of industries, aqueous coating compositions continue to replace traditional organic solvent-based coating compositions. Paints, inks, sealants, and adhesives, for example, previously formulated with organic solvents are now formulated as aqueous compositions. This reduces potentially harmful exposure to volatile organic compounds (VOC's) commonly found in organic solvent-based compositions. While the move from organic solvent-based to aqueous compositions brings health and safety benefits, the aqueous coating compositions must meet or exceed the performance standards expected from solvent-based compositions. The need to meet or exceed such performance standards places a premium on the characteristics and properties of such aqueous coating compositions.

U.S. Patent Nos. 5,668,273 and 5,994,530 disclose the use of carboxylalkyl cellulose esters, as well as their use in aqueous pigment dispersions and coating compositions. U.S. Patent No. 5,668,273 discloses various new ether derivatives of cellulose esters, which are described as being useful in coating compositions as binder resins and rheology modifiers. These esters are described as having good solubility in a wide range of organic solvents, compatibility with a variety of resins, and ease of dispersion in a water-borne formulation. U.S. Patent No. 5,994,530 describe carboxymethyl cellulose esters of higher acids that are used in aqueous dispersions, which are useful in formulating waterborne coating compositions containing pigments.

Methods of preparing carboxylalkyl cellulose esters are known in the art. For example, U.S. Patent Nos. 5,973,139; 5,792,856; and 4,590,265 describes carboxylated cellulose esters, and various synthetic processes for their preparation. U.S. Patent No. 5,973,139 describes a process which includes activating an oxidized cellulose with water, followed by dehydration using acetic acid, and optionally

displacing at least some of the acetic acid with butyric acid or propionic acid. The activated cellulose ester is then reacted with an esterifying reagent in the presence of a catalyst. The temperature is gradually increased to a level sufficient to complete the esterification. The carboxylated ester is then hydrolyzed to obtain the desired degree of substitution, and precipitated from solution.

U.S. Patent No. 5,792,856 describes a process for preparing carboxyalkyl cellulose esters. The process involves slurring water wet carboxy(C<sub>1</sub>-C<sub>3</sub> alkyl) cellulose (acid form) in a solvent, followed by treating the mixture with certain anhydrides in the presence of a strong acid catalyst. The mixture is heated to about 40° to 55°C until the reaction is complete. Next, a mixture of water, an alkanoic acid, and optionally a C<sub>2</sub>-C<sub>5</sub> alkanoic acid salt of an alkali or alkaline earth metal is added, in an amount that does not totally neutralize the strong acid catalyst. The solution is then heated to effect partial hydrolysis, and in an amount depending on the amount of strong acid catalyst, treated with a C<sub>2</sub>-C<sub>5</sub> alkanoic acid salt of an alkali or alkaline earth metal dissolved in water and an alkanoic acid.

U.S. Patent No. 4,590,265 relates to a method for the preparation of carboxylated cellulose esters, by reacting a cellulose ester with ozone at a temperature of about 25° to 80°C, for a period of time sufficient to yield the carboxylate cellulose ester product. The patent also discloses applications for the carboxylated cellulose esters, including metal coatings, pigment dispersions, wood coatings, and inks.

U.S. Patent No. 4,520,192 describes a process for preparing carboxyalkyl acetyl celluloses with a carboxyalkyl degree of substitution (DS) per anhydroglucose unit of 0.2-2.5 and an acetyl DS of 0.5-2.8 and the metal salts of these materials. The preparation of the carboxyalkyl acetyl cellulose is accomplished by converting carboxyalkyl cellulose, sodium salt, into its acid form by soaking in an aqueous acid solution of sulfuric acid, hydrochloric acid, nitric acid, or acetic acid. This is followed by washing with water, solvent exchange of the water with acetic acid, and reaction with acetic anhydride in the presence of a catalyst (sulfuric acid, perchloric acid, sulfoacetic acid or zinc chloride) to give a trisubstituted carboxy acetyl cellulose, *i.e.*, carboxymethyl cellulose acetate, upon precipitation into water. Also described is a process for converting the carboxyalkyl acetyl cellulose product (acid form) to its corresponding sodium, potassium, calcium, or ammonium carboxylate salt. The acid forms of the trisubstituted carboxyalkyl acetyl celluloses were insoluble in water and

aqueous lower chain alcohol solutions. These materials were soluble in acetone and methylene chloride/ethanol 9/1. The sodium salt of the carboxyalkyl acetyl cellulose was soluble in water, an aqueous lower alkyl alcohol containing a large amount of water, or aqueous acetone; however, it was insoluble in methylene chloride/ethanol 9/1. This process is believed to yield a product containing an unneutralized strong acid with high sulfur levels. Consequently, this ester would be unstable under general drying conditions or other heat treatment.

U.S. Patent No. 3,435,027 describes a base catalyzed (sodium hydroxide) esterification of carboxymethyl cellulose (in the sodium salt form) in 70-85% acetone nonsolvent media with acetic, propionic, lactic, or stearyl anhydride. The procedure yields a product with a low degree of ester substitution and falls well short of a fully substituted cellulose.

USSR Patent 612933 describes a process for preparation of cellulose acetate ethers wherein an alkali activated cellulose (12% sodium hydroxide) is etherified with monochloroacetic acid followed by esterification with acetic anhydride in the presence of sulfuric acid catalyst. The process is limited to a low DS of the carboxymethyl substituent.

U.S. Patent No. 3,789,117 discloses a process for preparing an enteric medicament coating from an organic solvent soluble cellulose derivative. The cellulose derivative's substitution has a carboxymethyl DS range of 0.3 to 1.2 in conjunction with at least one of the remaining hydroxyl groups being etherified or esterified. Ester groups include acetyl, propionyl, butyryl, nitric, or higher fatty acids. The degree of substitution is not specified.

RO 96929 (Romania) describes a carboxymethyl cellulose (CMC) acetate with a carboxymethyl degree of substitution of 0.5-3.0, acetyl DS of 0.4-2.9, and viscosity 150-1500 cP. This material was taught to be useful as an alkaline suspension stabilizer, solution thickener, and alkaline media binder. The material was prepared by mixing 70% acetic acid with CMC(Na salt), washing the acetic wet CMC with 50% acetic acid to remove the sodium acetate, and esterification of the acetic acid wet CMC--H with acetic anhydride for 1.5 hours at 50-110°C. in the presence of sulfuric acid.

U.S. Patent No. 5,008,385 reports cellulose derivatives that can be synthesized by homogeneous reaction in dimethylacetamide and/or N-methylpyrrolidine

containing LiCl. Included in their examples was CMC acetate (carboxymethyl DS 0.13-0.23, acetyl DS 2.54-2.15). These materials were tested for use in the production of fibers, filaments, or membranes.

Carbohydrate Research, 13, pp.83-88, (1970) describes the preparation of CMC acetate by sulfuric acid catalyzed acetylation of CMC (carboxymethyl DS of 0.07) hydrolysis (acetylation and hydrolysis procedures taken from Maim, Ind. Eng. Chem., 38 (1946) 77), and evaluation of this material in membranes for reverse osmosis.

Holzforschung, 27(2), pp. 68-70, (1973) describes the rate of carboxymethylation and deacetylation of cellulose acetate in the presence of sodium hydroxide. This work showed that deacetylation and carboxymethylation occur simultaneously with the rate of deacetylation being faster than the rate of carboxymethylation. The highest carboxymethyl DS obtained was less than 0.1.

GB 2,284,421 discloses carboxymethyl cellulose alkanoates which are "lightly carboxymethylated", *i.e.*, having a degree of substitution per anhydroglucose unit of less than 0.2. Such polymers are taught to be useful as a coating agent for paper and papermaking or as a bonding agent for non-woven fabric, or can be extruded to form filaments or film, or can be used to produce shaped articles.

Despite these developments in preparing carboxylalkyl cellulose esters and using them in coating applications, there remains a need for a process that improves adhesion of a stained wood substrate to an overcoat. Such a process would preferably impart one or more desirable characteristics to the substrate, such as reduced grain raising, increased wetting, increased adhesion with topcoats, improved brightness, good wiping, and good compatibility with additional overcoats and topcoats. The invention meets this need.

#### SUMMARY

The invention provides a method for making a stained wood substrate having an overcoat, with improved adhesion of the stained wood substrate to the overcoat. The process comprises the step of applying an aqueous carboxymethyl cellulose acetate butyrate (CMCAB) stain composition to a wood substrate, forming a stained wood substrate. The aqueous CMCAB stain composition contains CMCAB, optionally a colorant, water, and an organic solvent. The stained wood substrate is

then dried. Next, an overcoat is applied to the stained wood substrate, forming a coated, stained wood substrate. The coated, stained wood substrate is then cured.

This method for improving the adhesion of the stained wood substrate to an overcoat relates to a wide variety of wood substrates. Examples of wood substrates include, but are not limited to: oak, maple, yellow pine, birch, spruce, walnut, poplar, and aspen. Other wood substrates may also be used. The stained wood substrate that is formed will be compatible with a variety of overcoats, including, but not limited to: UV-curable overcoats, lacquer overcoats, acid-curable overcoats, nitrocellulose overcoats, thermoplastic overcoats, thermosetting overcoats, polyurethane overcoats, etc.

The method of the invention has the advantage of improving the adhesion of the stained wood substrate to an overcoat. Other advantages are reduced grain raising, increased wetting, increased adhesion with topcoats, and improved brightness. The stained wood substrate wipes well, and is compatible with a variety of colors, substrates, and overcoats.

The invention solves many of the existing problems with waterborne wood stains currently on the market. The replacement of the acrylic resin in the stain with a lesser total amount of CMCAB makes the waterborne stain behave more like a solventborne stain. It can be applied by a variety of methods known in the art, such as wiping with a rag, brushing, etc. If the CMCAB stain is applied by brush, it has the advantage of not gumming up the brush. In addition, the CMCAB stain raises the wood grain to a lesser extent and provides excellent adhesion to a wide variety of topcoats.

Various embodiments of the invention are described below. Any of the embodiments of the invention may be used either alone or taken in various combinations. Additional objects and advantages of the invention are discussed in the detailed description that follows, and will be obvious from that description, or may be learned by practice of the invention. It is to be understood that both this summary and the following detailed description are exemplary and explanatory only and are not intended to restrict the invention.

### DETAILED DESCRIPTION

This invention relates to a method for making a stained wood substrate having an overcoat, where the substrate displays improved adhesion of the stained wood substrate to the overcoat. The wood substrate formed by this method also exhibits reduced grain raising, increased wetting, increased adhesion with topcoats, and improved brightness. The stain wipes well, and is compatible with a variety of colors, substrates, and overcoats.

In a preferred embodiment, the invention is used with cellulosic wood substrates. Cellulose is a natural carbohydrate polysaccharide consisting of anhydroglucose units joined by an oxygen linkage to form long molecular chains, which are essentially linear. See Richard J. Lewis, Sr., *Hawley's Condensed Chemical Dictionary, Thirteenth Edition*, John Wiley & Sons, Inc., New York, 1997. The cellulose may be chemically modified, i.e. chemical groups (carboxyl, alkyl, acetate, nitrate, ether, etc.) may be substituted for the hydroxyl groups along the carbon chain.

The invention may also be practiced with a broad variety of substrates, made from various materials, such as wood, plastic, paper or cardboard. In a preferred embodiment, the invention relates to wood substrates. Examples of wood substrates include, but are not limited to: oak, maple, yellow pine, birch, spruce, walnut, poplar, and aspen. Other wood substrates may also be used, as well as various veneer substrates.

The process of the invention comprises the step of applying a carboxymethyl cellulose acetate butyrate (CMCAB) stain composition to the wood substrate to form a stained wood substrate. The CMCAB stain composition comprises CMCAB, and optionally one or more colorants, i.e. one or more organic or inorganic pigments and/or dyes, water and an organic solvent. In a preferred embodiment, the CMCAB stain composition will be applied as a wet coat, and contain about 12% solids, with pigment to binder in a ratio of about 0:1 to 2.5:1. In a preferred embodiment, the CMCAB stain composition will contain up to about 30% solids, up to about 15% solids, or about 10% solids. In another preferred embodiment, the CMCAB stain composition will be a natural stain without any colorants.

The aqueous CMCAB stain composition may be applied by any means known in the art. For instance, the CMCAB coating composition may be applied by spray,

wiping with a rag, or by painting with a brush or a roller. Other methods known in the art for applying a coating composition are also acceptable.

The CMCAB stain composition to be applied to the substrate will comprise certain esters of carboxy(C<sub>1</sub> -C<sub>3</sub> alkyl) cellulose, which are useful as components of coating compositions. Such esters preferably have an inherent viscosity of 0.20 to 1.7 dL/g, as measured in a 60/40 (wt./wt.) solution of phenol/tetrachloroethane at 25°C., a degree of substitution per anhydroglucose unit of carboxy(C<sub>1</sub> -C<sub>3</sub> alkyl) of about 0.20 to 0.75, and a degree of substitution per anhydroglucose unit of C<sub>2</sub> -C<sub>4</sub> esters of about 1.5 to about 2.7.

As a preferred embodiment, the CMCAB stain composition comprises a carboxymethyl cellulose acetate butyrate having a degree of substitution of carboxymethyl of 0.20 to 0.75, preferably 0.25 to 0.35, a degree of substitution per anhydroglucose unit of hydroxyl from about 0.10 to 0.70, and a degree of substitution per anhydroglucose unit of butyryl of about 0.10 to 2.60 and a degree of substitution per anhydroglucose unit of acetyl of 0.10 to 1.65, and having an inherent viscosity of 0.20 to 1.70 dL/g, as measured in a 60/40 (wt./wt.) solution of phenol/tetrachloroethane at 25°C. It is preferred that the degree of substitution per anhydroglucose unit of hydroxyl is 0.10 to 0.70, butyryl is 1.10 to 2.55, and acetyl is 0.10 to 0.90.

The C<sub>2</sub> -C<sub>4</sub> esters of carboxy(C<sub>1</sub> -C<sub>3</sub> alkyl) cellulose of the invention may be prepared by any method known in the art. As an example, they may be prepared by the following multi-step process. In this process, the free acid form of, for example, carboxy-methyl cellulose is water activated followed by water displacement via solvent exchange with an alkanoic acid such as acetic acid followed by treatment with a higher aliphatic acid (propionic acid or butyric acid) to give a carboxymethyl cellulose (CMC--H) activate wet with the appropriate aliphatic acid. In this regard, it is preferred that the starting carboxymethyl cellulose be prepared from cellulose with a 95 to 99% alpha content, preferably about 96 to 97% alpha cellulose content. The high alpha content is important for the quality of the final products prepared therefrom.

Next, the CMC--H is treated with the desired anhydride in the presence of a strong acid catalyst such as sulfuric acid to give a fully substituted carboxymethyl cellulose ester. A final solution (consisting of water and an aliphatic acid) is added

slowly to the anhydrous "dope" solution so as to allow removal of combined sulfur from the cellulose backbone. The final addition allows a slow transition through the hydrous point to give period of low water concentration and high temperature (as a result of the exotherm from water reacting with excess anhydride) in the reaction medium. This is crucial for hydrolysis of combined sulfur from the cellulose backbone. This product is then hydrolyzed using sulfuric acid to provide a partially substituted carboxymethyl cellulose ester. Hydrolysis is necessary to provide gel free solutions in organic solvents and to provide better compatibility with other resins in coatings applications.

Next, the sulfuric acid is neutralized after the esterification or hydrolysis reactions are complete by addition of a stoichiometric amount of an alkali or alkaline earth metal alkanoate, for example, magnesium acetate, dissolved in water and an alkanoic acid such as acetic acid. Neutralization of the strong acid catalyst is important for optimal thermal and hydrolytic stability of the final product.

Finally, either the fully substituted or partially hydrolyzed forms of carboxy(C<sub>1</sub> -C<sub>3</sub> alkyl) cellulose ester are isolated by diluting the final neutralized "dope" with an equal volume of acetic acid followed by precipitation of the diluted "dope" into a volume of water about 1.5 to 3.0 times its weight. This is followed by addition of 1.5 to 3.0 volumes of water to give a particle that can be easily washed with de-ionized water to efficiently remove residual organic acids and inorganic salts. As an alternative isolation, the fully substituted or partially hydrolyzed forms of carboxy(C<sub>1</sub> -C<sub>3</sub> alkyl) cellulose ester are isolated by precipitation of the diluted dope by addition of about 2.0 times its volume of 10% aqueous acetic acid, followed by an additional 2.0 times the dope volume of water.

As a preferred embodiment of this process, the reaction mixture is diluted with an equal volume of acetic acid, followed by precipitation of the diluted product into a volume of water about 1.5 to 3.0 times its weight, followed by an additional volume of water about 1.5 to 3.0 times its weight, washed with deionized water and dried to provide the desired product as a powder or granules. This powder is thus free from any significant amount of residual organic acids and inorganic salts.

As an alternative embodiment of this process, the reaction mixture is diluted with an equal volume of acetic acid, followed by precipitation of the diluted product by the addition of about 2.0 times its volume of aqueous acetic acid, followed by about 2.0 times its volume of water, washed with deionized water and dried to provide the desired product as a powder.

The CMCAB stain composition may optionally contain one or more colorants, i.e. one or more organic or inorganic pigments and/or dyes, including extender pigments. Any colorants known to one of ordinary skill in the art may be used. Typical white pigments include titanium dioxide, zinc oxide, zinc sulfide, white lead, lithophone, and modifications thereof. Black pigments are selected from the group of mineral blacks, bone blacks, iron oxide blacks, and carbon blacks, for example. Inorganic colored pigments include lead chromates, metal oxides, sulfides and sulfoselenides, iron blue, cobalt blue, ultramarine blue, manganese violet, bismuth vanadate, and molybdate yellow, for example. Examples of organic colored pigments include metallized azo reds including lithol reds, permanent red 2B, lithol rubine red, BON reds, BON maroon-nonmetallized azo reds including toluidine red, para reds, napthol reds, quinacridone reds, vat reds, anthraquinone red, brominated pyranthrone red, perylene reds, benzimidazolon based reds, diazo condensation reds, thioindigoid reds, pigment red 251, 252, and 257. Blue pigments include, but are not limited to, copper phthalocyanine blues, indanthrone blue, and carbazole violet. Examples of yellow pigments include monoarylide yellows, diarylide yellows, benzimidazolone yellows, and heterocyclic yellows. Orange pigments include azo-based oranges, bisazo-based oranges, bisazo condensation-based oranges, perinone type orange, quinacridone type orange, pyranthrone type orange, heterocyclic hydroxy-based orange, and pyrazoloquinazolone-based orange. Examples of green pigments include copper phthalocyanine greens, and triphenylmethane-phospho tungsto molybdic acid (PTMA) complexes. Extender pigments include calcium carbonate, kaolin or china clay, talc, silica, mica, barium sulfate, wollastonite, sodium aluminosilicates, alumina trihydrate, and aluminum oxide. Metallic Pigments include, but are not limited to, aluminum, zinc, gold, bronze, nickel, and stainless steel. Examples of pearlescent pigments, include titanium dioxide and ferric oxide coatings on mica, bismuth oxychloride crystals grown from a solution of bismuth salts, natural pearl essence,

guanine, and hypoxanthane purines from fish scales. This list is not meant to be exclusive.

Dyes that might be used are included in the following classes, *i.e.*, Acid dyes, Azoic Coupling Components, Azoic Diazoic Components, Basic dyes, Direct Dyes, Reactive dyes, Solubilized Vat Dyes, Solvent Dyes, Sulfur Dyes, Vat Dyes, and Aniline Dyes. Specific dyes by C.I. number and dyes of both domestic and foreign manufacture can be found in the Colour index and its Additions and Amendments, published jointly by the American Association of Textile Chemist and Colorists, Research Triangle Park, NC and The Society of Dyers and Colourists in Bradford, England. Other suitable pigments and dyes are known in the art. Pigment dispersions may be prepared by blending the cellulose ester and a pigment with heat and/or shear to disperse the pigment. In this manner, pigments can be easily dispersed in coating formulations, thereby providing high coloring power and good transparency while using a minimal amount of pigment.

Mixtures of carboxymethylcellulose (CMC) esters and pigments may be prepared at pigment to ester ratios of from about 10:90 to about 90:10 weight percent. In a high shear environment, such as when using organic pigments, it is preferable to use pigments in an amount from about 10 to 20 weight percent, and esters in an amount from about 90 to 80 weight percent. These dispersions may be prepared on two-roll mill, ball mill, Kady mill, sand mill, Cowles mixers, and the like. For pigments requiring gentle agitation or prepared in a low shear environment, the pigments may be present in an amount from about 50 to 90 weight percent and the C<sub>2</sub>-C<sub>4</sub> esters of carboxy(C<sub>1</sub>-C<sub>3</sub> alkyl) cellulose in an amount from about 50 to 10 weight percent. A typical pigment dispersion may be formed by blending either a solution or a dispersion of the esters with the pigment with the necessary shear required in order to disperse the pigment.

The coatings may be applied to a substrate in the form of an organic solvent solution, an amine neutralized waterborne dispersion, a fully neutralized aqueous/organic colloidal dispersion, or as a zero VOC-exempt solvent dispersion in acetone with aqueous ammonia. The coatings may also act as a protective coating for a variety of substrates, especially metal and wood.

Some examples of typical solvents include: acetone, methyl ethyl ketone, methyl isobutyl ketone, methyl amyl ketone, methyl isoamyl ketone, 2-propoxy-

ethanol, 2-butoxyethanol, ethyl 3-ethoxypropionate, 2-butanone, methanol, ethanol, propanol, isopropyl alcohol, butanol, 2-ethyl-hexanol, ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate, isobutyl acetate, ethyl ether, propyl ether, propyl glycol butyl ether, diethylene glycol methyl ether, diethylene glycol ethyl ether, diethylene glycol butyl ether, dipropylene glycol ether, dipropylene glycol methyl ether, ethylene glycol, ethylene glycol butyl ether, ethylene glycol diethyl ether, ethylene glycol dimethyl ether, ethylene glycol ethyl ether, ethylene glycol 2-ethylhexyl ether, ethylene glycol methyl ether, ethylene glycol phenyl ether, 1-methyl-2-pyrrolidinone, ethylene glycol diacetate, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether, ethylene glycol monobutyl ether, ethyl ether, propylene glycol butyl ether, propylene glycol dimethyl ether, propylene glycol ethyl ether acetate, propylene glycol methyl ether, propylene glycol ethyl ether, propylene glycol propyl ether, propylene glycol butyl ether, propylene glycol methyl ether acetate, propylene glycol phenyl ether, propylene glycol propyl ether, propylene glycol, tripropylene ethyl ether, triethylene glycol, tri(ethylene glycol) dimethyl ether, and mixtures thereof.

Other volatile inert solvents typically used in coating compositions may also be added, as will be apparent to one of ordinary skill in the art. Typically, the amount of solvent will be adjusted in order to dissolve and/or suspend the various components of the composition in a uniform liquid suspension or liquid. As an example, organic solutions of the esters of this invention may be prepared by adding 1 to 1000 parts of solvent per part of ester; 1.5 to 9 parts of solvent per part of ester is preferred. In an embodiment of the invention, the CMCAB stain composition will be aqueous, which will reduce VOCs.

In certain instances, minor amounts of an organic solvent may help to reduce grain raising. Grain raising results in the roughening of the surface of the wood substrate. It is usually initiated by the absorption of moisture or water, which is absorbed by cellulosic material in the wood cell wall. Because the amount of cell wall substance varies across the wood substrate, variations in the amount of moisture/water absorption takes place resulting in differential swelling and shrinking hence resulting in a grain raised or roughened surface. However, the amounts of organic solvents are generally minimized in order to minimize volatile organic

content (V.O.C.). Preferred embodiments of the compositions of the invention have V.O.C. less than 3 g/gallon, most preferably less than 2.6 g/gallon.

The CMCAB esters used in the invention possess free hydroxyl groups and thus can also be utilized in conjunction with crosslinking agents such as melamines and isocyanates. Such melamines are preferably compounds having a plurality of --N(CH<sub>2</sub>OR)<sub>2</sub> functional groups, wherein R is C<sub>1</sub>-C<sub>4</sub> alkyl, preferably methyl. In general, the melamine cross-linking agent may be selected from those known in the art. Examples of crosslinking agents include hexamethoxymethylmelamine, tetramethoxymethylbenzoguanamine, tetramethoxymethylurea, mixed butoxy/methoxy substituted melamines, and the like. The most preferred melamine cross-linking agent is hexamethoxymethylmelamine and urea-formaldehyde. Typical isocyanate crosslinking agents and resin include hexamethylene diisocyanate (HMDI), isophorone diisocyanate (IPDI), and toluene diisocyanate, and their adducts.

Since there are free --COOH groups present on the CMCAB esters, one could use the usual crosslinkers and resins used with carboxyl functional resins, e.g., epoxy resins or glycidyl-functional resins. Preferred epoxy functional resins generally have a molecular weight of about 300 to about 4000, and have approximately 0.05 to about 0.99 epoxy groups per 100 g of resin (*i.e.*, 100-2000 weight per epoxy (WPE)). Such resins are widely known and are commercially available under the EPON™ trademark of the Shell Chemical Company, the ARALDITE™ trademark of CIBA-Geigy, and D.E.R. resins of the Dow Chemical Company. Other examples of resins include polyester resins, including water extended polyesters, polystyrene, vinyl resins including polyvinylacetate, polyvinylchloride, vinylchloride-vinylacetate copolymers and the like; polyamide resins, polyurea resins, and acrylic resins; phenolic resins, maleic resins, coumerone-indene resins, urea-formaldehyde; melamine-formaldehyde resins; epoxy resins, silicone resins, ionomer resins, acetal resins, polyethylene, polypropylene, hydrocarbon resins, rubber derivatives, polycarbonate resins, phenoxy resins, fluorol plastics, styrene-butadiene resins, polyurethane resins, furane resins, polysulfone resins, pentaerythritol resins, ester gum, co-polyesters, UV-curable oligomers with corresponding photoinitiators, and the like. Natural resins which may be used include shellac, rosin, copal resins, damar resins, manila resins and the like.

As a further aspect of the invention, the above compositions are further comprised of one or more coatings additives. Such additives are generally present in

a range of about 0.1 to 15 weight percent, based on the total weight of the composition. Examples of such coatings additives include waxes, leveling, flow control agents and rheology modifiers such as silicones, clays, fluorocarbons, cellulosics, and organic rheology modifiers such as acrylics, and mixtures thereof; flattening agents; pigment wetting and dispersing agents; surfactants; ultraviolet (UV) absorbers; UV light stabilizers; tinting pigments; defoaming and antifoaming agents; anti-settling, anti-sag and bodying agents; anti-skinning agents; anti-flooding and anti-floating agents; fungicides and mildewcides; corrosion inhibitors; thickening agents; or coalescing agents. Specific examples of additional coatings additives can be found in Raw Materials Index, published by the National Paint & Coatings Association, 1500 Rhode Island Avenue, N.W., Washington, D.C. 20005.

Examples of flattening agents include synthetic silica, available from the Davison Chemical Division of W. R. Grace & Company under the trademark SYLOID™; polypropylene, available from Hercules Inc., under the trademark HERCOFLAT™; synthetic silicate, available from J. M Huber Corporation under the trademark ZEOLEX™.

Coating compositions of the invention may also contain any compatible plasticizer known in the art. Examples of plasticizers include, but are not limited to, texanol isobutyrate, diisononyl phthalate, dioctyl phthalate, butyl benzyl phthalate, dibutyl phthalate, diethylene glycol, dioctyl terephthalate, and mixtures thereof. Other preferred plasticizers include TXIB (Texanol Isobutyrate, commercially available from Eastman Chemical Company), DINP (Diisononyl Phthalate, commercially available from Exxon Mobile Chemical Company), DOP (Diethyl Phthalate, commercially available from Eastman Chemical Company), BBP (Butyl Benzyl Phthalate, commercially available from Solutia, Inc.), DBP (Dibutyl Phthalate, commercially available from Eastman Chemical Company), EMN-425 (a blend of 75/25 DOTP/Benzoate ester, commercially available from Eastman Chemical Company), DOA (dioctyl adipate), and TEG-2EH (triethylene glycol di-2-ethylhexanoate).

Examples of dispersing agents and surfactants include sodium bis(tridecyl) sulfosuccinate, di(2-ethyl hexyl) sodium sulfosuccinate, sodium dihexylsulfosuccinate, sodium dicyclohexyl sulfosuccinate, diamyl sodium sulfosuccinate, sodium diisobutyl sulfosuccinate, disodium iso-decyl sulfosuccinate, disodium ethoxylated alcohol half ester of sulfosuccinic acid, disodium alkyl amido polyethoxy sulfosuccinate, tetra-sodium N-(1,2-dicarboxyethyl)-N-octadecyl sulfosuccinamate, disodium N-octasulfo-succinamate, sulfated ethoxylated nonylphenol, 2-amino-2-methyl-1-propanol, and the like.

Examples of viscosity, suspension, and flow control agents include polyaminoamide phosphate, high molecular weight carboxylic acid salts of polyamine amides, and alkyl amine salt of an unsaturated fatty acid, all available from BYK Chemie U.S.A. under the trademark ANTI TERRA™. Further examples include polysiloxane copolymers, polyacrylate solution, cellulose esters, hydroxyethyl cellulose, hydrophobically-modified hydroxyethyl cellulose, hydroxypropyl cellulose, polyamide wax, polyolefin wax, carboxymethyl cellulose, ammonium polyacrylate, sodium polyacrylate, and polyethylene oxide.

Several proprietary antifoaming agents are commercially available, for example, under the trademark BRUBREAK of Buckman Laboratories Inc., under the BYK™ trademark of BYK Chemie, U.S.A., under the FOAMASTER™ and NOPCO™ trademarks of Henkel Corp./Coating Chemicals, under the DREWPLUS™ trademark of the Drew Industrial Division of Ashland Chemical Company, under the TROYSOL™ and TROYKYD™ trademarks of Troy Chemical Corporation, and under the SAG™ trademark of Union Carbide Corporation.

Examples of fungicides, mildewcides, and biocides include 1,2-benzisothiazolin-3-one, 4,4-dimethyloxazolidine, 3,4,4-trimethyloxazolidine, modified barium metaborate, potassium N-hydroxy-methyl-N-methyldithiocarbamate, 2-(thiocyanomethylthio) benzothiazole, potassium dimethyl dithio-carbamate, adamantine, N-trichloro-methylthio) phthalimide, 2,4,5,6-tetra-chloroisophthalonitrile, orthophenyl phenol, 2,4,5-trichlorophenol, dehydroacetic acid, copper naphthenate, copper octoate, organic arsenic, tributyl tin oxide, zinc naphthenate, and copper 8-quinolinate.

Examples of U.V. absorbers and U.V. light stabilizers include substituted benzophenone, substituted benzotriazole, hindered amine, and hindered benzoate,

available from American Cyanamide Company under the tradename Cyasorb UV, and available from Ciba Geigy under the trademark TINUVIN, and diethyl-3-acetyl-4hydroxy-benzyl-phosphonate, 4-dodecyl-oxy-2-hydroxy benzophenone, and resorcinol monobenzoate.

After the aqueous CMCAB stain composition is applied, the stained wood substrate is then dried by any means known in the art. Typical drying methods include providing combinations of heat and/or air and/or UV light in order to speed the rate of drying.

Next, according to the invention one or more overcoats are applied to the stained wood substrate. Examples of overcoats include, but are not limited to, UV-curable clearcoats, lacquers, acid cures, nitrocellulose coatings, etc. The overcoat may be applied by any acceptable method known in the art, i.e. application by spraying or coating. In addition, the overcoat, in the form of a powder, may be sprayed onto the substrate by well known electrostatic powder spray techniques, such as corona discharge or triboelectric electrostatic spray techniques. After the overcoat is applied, the stained, coated substrate is cured.

As mentioned above, the coated, stained substrate produced according to the invention will exhibit improved adhesion of the stained wood substrate to an overcoat. Other advantages are reduced grain raising, increased wetting, increased adhesion with topcoats, and improved brightness. The stain produced by the method of the invention wipes well, and is compatible with a variety of colors, substrates, and overcoats.

## EXAMPLES

The practice of the invention is disclosed in the following examples, which should not be construed to limit the invention in any way.

### Preparation of CMCAB Esters

CMCAB esters usable in this invention may be prepared as described in U.S. Patent No. 5,994,530, which is hereby incorporated in its entirety. The CMCAB esters used in the following examples were prepared according to the following description.

Carboxymethyl cellulose, sodium salt form (CMC—Na), (approximately 0.35 DS carboxymethyl based on final product calculations) was converted to the free acid

(CMC—H) by adding 100 grams of CMC—Na)(about 70% CMC—Na by wt.) to 2100 grams of about 2% to about 6% sulfuric acid. After about 2 to 5 minutes, the sample was filtered free of excess liquids and washed with demineralized water. The protonated CMC—H was transferred to a glass fritted funnel and excess water removed. The activate was dewatered by solvent exchange with three 250 gram portions of acetic acid and three 250 gram portions of butyric acid to give butyric acid wet CMC—H activate (about 15 to 40 wt % solids). The activate was transferred to a 2 liter round bottom flask and chilled in ice for 1 hour. The activate was esterified by treating with 264 grams of butyric anhydride, 30 grams of acetic anhydride, and 2.94 grams of sulfuric acid at 0°C. The reaction was allowed to warm as a result of the exotherm and proceeded to dissolution after 2.1 hours at 45° C. (additional heat was required to hold the temperature at 43° C.). A solution of 74 grams of water and 74 grams of acetic acid was added dropwise to the reaction mixture over 30 minutes generating an exotherm of approximately 15° C. as a result of reaction of excess anhydride with water. The contents were hydrolyzed by heating to 60° C. for 4.5 hours. The sulfuric acid catalyst was then neutralized by the addition of 7.1 grams of magnesium acetate (tetrahydrate) in 20 mL of water and 19 mL of acetic acid. The reaction contents were diluted with an equal weight of acetic acid and precipitated by adding 3,000 mL of 10% aqueous acetic acid. The precipitated particles were hardened by the addition of 3,000 mL of water. The contents were filtered, washed with de-ionized water, and dried to obtain 106 grams of the protonated form of carboxymethyl cellulose acetate butyrate as a white granular powder: GC % acetyl 6.38, GC % butyryl 39.52%; acid number 58.0; PPM sulfur 39; molecular weight number average 84,700; inherent viscosity (IV) 1.02 dL/g (60/40 wt./wt. solution of phenol/tetrachloroethane at 25° C). Calculation for degree of substitution (DS) gives: carboxymethyl 0.35, acetyl 0.50, butyryl 1.88, and hydroxyl 0.27. A highly preferred method for preparation of CMCA esters is as follows:

*1. Conversion of carboxymethyl cellulose-sodium salt to the acid form:*

CMC—Na was converted to the free acid by the addition of 100 grams of carboxymethyl cellulose to 2-16% aqueous sulfuric acid at 27-60° C. The solids content of the resulting slurry was about 6%. The slurry was stirred for about 15 minutes and the acid solution was filtered to recover CMC—H.

**2. Activation of CMC (CMC—H):**

CMC—H was washed in water with stirring for 5 minutes to 1 hour. The water was drained to approximately 20% solids. The water-wet CMC—H was dewatered by washing 3 times with 200-500 grams of acetic acid followed by 3 washes with 200-500 grams of butyric acid. In between each wash the sample was drained to approximately 16-18% solids. After the final butyric acid wash, vacuum was applied to obtain the butyric acid wet CMC—H activate at 15-40% solids.

**3. Esterification:**

The butyric acid wet CMC—H was combined with 31 grams of acetic anhydride, and 253 grams of butyric anhydride at 0° C. A catalyst solution consisting of 3.44 grams of sulfuric acid in 3.44 grams of acetic acid was added slowly to the reaction mixture keeping the temperature below 30° C. After completion of the catalyst addition, the temperature was ramped from 30° C. to 35° C. over 150 minutes. The temperature was then ramped from 35° to 45° C. over a 60 minute period. The reaction mass was heated at 45° C. until complete dissolution of the solids to an acid dope.

**4. Hydrolysis:**

A solution of 95 grams of water and 95 grams of acetic acid was added to the acid dope over 30-45 minutes at 40-45° C. thereby adjusting the water concentration to 13-14%. The temperature was increased to 70° C. and held for 2 hours. Then, 7.53 grams of magnesium acetate (tetrahydrate) in 25 grams of water and 25 grams of acetic acid was added to neutralize the strong acid catalyst.

**5. Filtration:**

The resulting dope was diluted with acetic acid and water to give about a 1:1 ratio of acetyl/butyryl and approximately 20% water concentration. The acid dope was held at 65° C. and circulated through a 0.5 micron filter to remove any particulates.

#### *6. Precipitation:*

The dope from above was added to water with agitation to give a flake precipitate. This material was allowed to harden, washed with water, and dried at 60° C. An optional precipitation method is to add 10% aqueous acetic in sufficient volume to yield about 30% organic acid in the final precipitation bath followed by the addition of an equal amount of water. The precipitate is then washed with water and dried at 60° C. This yields a CMCA ester with the following general analysis (methods of analysis described below): Acid number 55-60, PPM Sulfur 25-100 PPM, IV (60/40 (wt./wt.) solution of phenol/tetrachloroethane at 25° C.) 0.5-0.7 dL/g, DS of carboxymethyl groups 0.30-0.35, acetyl 0.4-0.6, butyryl 1.7-2.05, and hydroxyl of 0.1-0.6.

#### Determination of Acid Number

The acid number of a carboxy(C<sub>1</sub>-C<sub>3</sub> alkyl) cellulose ester is determined by titration as follows. An accurately weighted aliquot (0.5-1.0 g) of the carboxy(C<sub>1</sub>-C<sub>3</sub> alkyl) cellulose ester was mixed with 50 mL of pyridine and stirred. To this mixture was added 40 mL of acetone followed by stirring. Finally, 20 mL of water was added and the mixture stirred again. This mixture was titrated with 0.1N sodium hydroxide in water using a glass/combination electrode. A blank consisting of 50 mL pyridine, 40 mL of acetone and 20 mL water was also titrated. The acid number was calculated as follows where:

Ep=mL NaOH solution to reach end point of sample

B=mL NaOH solution to reach end point of blank

N=normality of sodium hydroxide solution

Wt.=weight of carboxy(C<sub>1</sub>-C<sub>3</sub> alkyl) cellulose ester titrated

Acid Number (mg KOH/g sample)=((Ep-B)\*N\*56.1)/Wt.

#### Determination of acetyl, propionyl, and butyryl Weight Percents

The acetyl, propionyl, and butyryl weight percents were determined by a hydrolysis GC method. In this method, about 1 g of ester was weighed into a weighing bottle and dried in a vacuum oven at 105° C. for at least 30 minutes. Then 0.500+/-0.001 g of sample was weighed into a 250 mL Erlenmyer flask. To this flask was added 50 mL of a solution of 9.16 g isovaleric acid, 99%, in 2000 mL pyridine. This mixture was heated to reflux for about 10 minutes after which 30 mL of

methanolic potassium hydroxide solution was added. This mixture was heated at reflux for about 10 minutes. This mixture was allowed to cool with stirring for 20 minutes and then 3 mL of concentrated hydrochloric acid was added. The mixture was stirred for 5 minutes and then allowed to settle for 5 minutes. About 3 mL of solution was transferred to a centrifuge tube and centrifuged for about 5 minutes. The liquid was analyzed by GC (split injection and flame ionization detector) with a 25M×0.53 mm fused silica column with 1 micron FFAP phase. The weight percent acyl was calculated as follows where:

C<sub>i</sub>=concentration of I(acyl group)

F<sub>i</sub>=relative response factor for component I

F<sub>s</sub>=relative response factor for isovaleric acid

A<sub>i</sub>=area of component I

A<sub>s</sub>=area of isovaleric acid

R=(grams of isovaleric acid)/(g sample)

C<sub>i</sub>=((F<sub>i</sub>\*A<sub>i</sub>)/F<sub>s</sub>\*A<sub>s</sub>)\*R\*100

This GC method was used instead of NMR because the methylene of the carboxymethyl group cannot be separated from the ring protons of the cellulose backbone making absolute DS measurements by NMR difficult. The DS values were calculated by converting the acid number to percent carboxymethyl.

## Formulations

### *Formulation A:*

The CMCAB dispersion was made by mixing 563.81 g EB (ethylene glycol butyl ether, commercially available from Eastman Chemical Company), and 241.63 g of CMCAB for 30 minutes, until dissolved. Next, 5.96 g of AMP-95 (2-amino-2-methyl-1-propanol) was added, followed by the slow addition of 1188.60 g of distilled water, added at a rate of approximately 4 teaspoons at a time. The pH of the resulting dispersion was about 4.70. Formulation A is summarized in Table 1, below.

*Table 1. Formulation A (CMCAB Dispersion – Approx. 2000 Grams)*

Items	Wt/grams	Wt%
ethylene glycol butyl ether	563.81	28.19
CMCAB	241.63	12.08
<b>MIX 30 MINS UNTIL DISSOLVED</b>		
AMP-95	5.96	0.30
<b>Add slowly (approx. 4 tsp. at a time)</b>		
Distilled water	1188.60	59.43
<b>Total</b>	<b>2000</b>	<b>100</b>
pH	4.70	

*Formulation B:*

A LAPONITE RDS™ thickener solution was made by mixing 171 g of tap water with 19 g of LAPONITE RDS™ (commercially available from Southern Clay Products, Inc. Gonzales, Texas), until clear and homogeneous. Formulation B is summarized in Table 2, below.

*Table 2. Formulation B (Laponite RDS™ Thickener Solution)*

Item	Wt/grams
Tap Water	171
LAPONITE RDS™	19
<b>MIX UNTIL CLEAR AND HOMOGENEOUS</b>	

*Formulation C:*

Approximately 3700 g of aqueous CMCAB-based stain was made by mixing 1640.87 g distilled water, 86.33 g of Formulation B, and 68.66 g of ACRYSOL SCT 275 Thickener™ (commercially available from Rohm and Haas Co., Philadelphia, PA). Next, 803.07 g of Formulation A was added, and the formulation was mixed. Next, 484.45 g of ELEMENTIS' TINT-AYD CW5509™ (commercially available from Elementis Specialties, Jersey City, NJ) was added, and the formulation was mixed. Then, 616.62 g of propylene glycol was added, and the formulation was mixed.

Viscosity was measured using a #2 Zahn dip cup, signature series at 74°F. Batch (i) had a viscosity of 17.34 seconds (under agitation), while Batch (ii) had a viscosity of 18.91 seconds (without agitation). Batch (i) and (ii) had a pH of about

7.41 and 7.42, respectively. Both batches were slow to gravity filter. Formulation C is summarized in Table 3, below.

*Table 3. Formulation C (CMCAB Stain)*

Item	WT/GRAMS	
	Batch (i)	Batch (ii)
Distilled Water	1640.87	1640.87
Formulation B	86.33	86.33
SCT 275™ Thickener	68.66	68.66
<b>MIX THEN ADD</b>		
Formulation A (CMCAB Dispersion)	803.07	803.07
<b>MIX THEN ADD</b>		
ELEMENTIS' CW5509™	484.45	484.45
<b>MIX THEN ADD</b>		
Propylene Glycol	616.62	616.62
<b>MIX</b>		
Viscosity	17.34 sec, (under agitation)	18.91 sec, (not under agitation)
pH	7.41	7.42
Filter 50 micron	Both slow to gravity filter	
Comments	Slight stuff in bottom	

#### *Formulation D:*

The CMCAB dispersion was made by mixing 140 g EB (ethylene glycol butyl ether, commercially available from Eastman Chemical Company), and 60 g of CMCAB for 30 minutes, until dissolved. Next, 1.48 g of AMP-95 (2-amino-2-methyl-1-propanol) was added, followed by the slow addition of 295.14 g of distilled water. The formulation was filtered through nylon mesh. Formulation D is summarized in Table 4, below.

*Table 4. Formulation D*

Item	Wt/grams
EB	140
CMCAB	60
<b>MIX 30MIN, THEN ADD</b>	
AMP-95™	1.48
<b>MIX, THEN ADD VERY SLOWLY</b>	
Distilled water	295.14
Filter through nylon mesh	

***Formulation E:***

The formulation was made by mixing 245.198 g of distilled water, 12.9 g of Formulation B, and 10.26 g of ACRYSOL SCT-275™ (commercially available from Rohm and Haas Co, Philadelphia, PA). Next, 120.0 g of Formulation D was added, with mixing. Next, 77.39 g of TINT-AYD CW5509™ (commercially available from Elementis Specialties, Jersey City, NJ) was added and mixed. The resulting formulation had a viscosity of 18.22 when measured using a #2 Zahn dip cup, signature series at 77°F. Formulation E is summarized in Table 5, below.

*Table 5. Formulation E*

Item	Wt/grams
Distilled water	245.19
Formulation B	12.9
ACRYSOL SCT-275	10.26
<b>MIX THEN ADD</b>	
Formulation D (CMCAB dispersion)	120.0
<b>MIX THEN ADD</b>	
TINT-AYD CW5509™	72.39
<b>MIX</b>	
Total	460.74
Viscosity, #2Zahn dip cup, Signature Series at 77°F	18.22 seconds
pH	7.07

***Formulation F:***

Formulation F was prepared by combining 151.07g of Formulation E, and 30.21 g of propylene glycol. The resulting formulation had a pH of about 7.19, and a viscosity of 16.66 when measured using a #2 Zahn dip cup, signature series at 78°F. Formulation E is summarized in Table 6, below.

*Table 6. Formulation F*

Item	Wt/grams
Formulation E	151.07
Propylene Glycol	30.21
pH	7.19
Viscosity, #2Zahn dip cup, Signature Series @78F	16.66 seconds

***Formulation G:***

Formulation G was prepared by combining 70g of ethylene glycol butyl ether and 30g of CMCAB, and mixing for thirty minutes. Next, 0.74 g of AMP-95 (2-amino-2-methyl-1-propanol) was added, followed by the slow addition of 147.57 g of distilled water. The pH of the resulting dispersion was about 5.3-5.4. Formulation G is summarized in Table 7, below.

*Table 7. Formulation G*

Item	Wt/grams
Ethylene glycol butyl ether	70
CMCAB	30
<b>MIX 30MIN, THEN ADD</b>	
AMP-95	0.74
<b>MIX, THEN ADD UNDER GOOD AGITATION VERY SLOWLY</b>	
Distilled water	147.57
<b>Total</b>	<b>248.31</b>
pH	5.3/5.4

***Formulation H:***

A clear base was made by mixing 353.04 g distilled water, 0.54 g of PROXEL GXL™ (1,2-benzisothiazolin-3-one), and 1.77 g NATROSOL PLUS 330PA™ (commercially available from Aqualon, Wilmington, DL) until dissolved. Next 164.97 g of Formulation G was added. Formulation H is summarized in Table 4 below:

*Table 8. Formulation H (Clear Stain Base for Various Pigment Dispersion Evaluations)*

Item	WT/GRAMS
Distilled Water	353.04
PROXEL GXL	0.54
NATROSOL PLUS 330PA	1.77
<b>MIX UNTIL DISSOLVED</b>	
Formulation G	164.97

***Formulation I:***

Formulation I was prepared by combining 46.0g of distilled water, 41.20 g DISPERBYK 190™ (commercially available from Byk Chemie, Wallingford, CT),

2.0 g of BYK 019 (commercially available from Byk Chemie, Wallingford, CT), and 0.15

g of PROXEL GXL™ (1,2-benzisothiazolin-3-one). The formulation was mixed, and then AEROSIL 200™ (commercially available from Degussa Corp., Akron, OH) and Burnt Umber 5250 (commercially available from Harcross Pigments, Fairview Heights, IL) were dispersed at high speed for twenty minutes. Finally, 20.05 g of distilled water was added. Formulation I is summarized below, in Table 9.

*Table 9. Formulation I*

<b>Formulation I (B4P424A)</b>	
<b>Item</b>	<b>Wt/grams</b>
Distilled water	46.0
DISPERBYK 190™	41.20
BYK 019™	2.0
PROXEL GXL™	0.15
<b>MIX, THEN ADD</b>	
AEROSIL 200™	0.6
BURNT UMBER 5250™	110
<b>DISPERSE, HIGH SPEED, 20MIN</b>	
Grind	Off gage
<b>ADD</b>	
Distilled water	20.05

***Formulations J—Q:***

Formulation J-Q were made as summarized in Table 10.

*Table 10. CMCAB Aqueous Stain Formulations Evaluating Commercial Pigment Dispersions*

<b>Formulation:</b>	<b>FORMULATION, WT/GRAMS</b>							
	<b>J</b>	<b>K</b>	<b>L</b>	<b>M</b>	<b>N</b>	<b>O</b>	<b>P</b>	<b>Q</b>
Formulation H Clear Base	60	60	60	60	60	60	60	60
Formulation I Pigment Dispersion	9.19							
Sunperse white WHD 9507™		6.99						
Sunperse Red Oxide RHD 9584™			8.87					
RBH White 509901™				7.06				
Creonova white 877-0019™					6.50			
Hilton Davis/BFG white 13463-07-7™						7.55		
Daniels/Elementis BU CW5509™							11.48	
Daniels/Elementis white CW5003™								7.03
Approximate P/B (pigment to binder ratio)	2/1	no data from vendor	no data from vendor	2/1	2/1	2.1/1	2/1	2.1/1
Comments			Some lumps remain after mixing		Very low hiding			
Syneresis after overnight	Essenti-ally none	Essenti-ally none	Slight	Lots	Lots	Essenti-ally none	None	Essenti-ally none
Settling after overnight	None	Essenti-ally none	None	None	None	None	None, very thixo	None
Syneresis after approx. 10 days, RT	None	Trace	Slight to moderate	Lots	Lots	Slight	Essenti-ally none	moder-ate
Settling after approx. 10 days, RT	None; sample v. thixo. But smooth and no flocculation	Trace. V. soft; acceptable	v. slight, v. soft, v. easily stirred	v. soft, v. easily stirred	v. soft, easily stirred, but not quite as easy as D	v. soft; v. easily stirred	None, very thixo	v. soft. V. easily stirred

Sunperse WHD 9507™ is commercially available from Sun Chemical Corporation, Cincinnati, OH; Sunperse RHD 9584™ is commercially available from Sun Chemical Corporation, Cincinnati, OH; RBH 509901™ is commercially available from Hilton Davis/B.F. Goodrich, Cincinnati, OH; Creanova 877-0019™ is commercially available from Creanova, Somerset, NJ; BFG 13464-07-7™ is commercially available from Hilton Davis/B.F. Goodrich, Cincinnati, OH; Tint-Ayd CW5509™ is commercially available from Elementis Specialties, Jersey City, NJ; and Tint-Ayd CW5003™ is commercially available from Elementis Specialties, Jersey City, NJ.

### Tests

#### **NICKEL ADHESION TEST**

The Nickel adhesion test was conducted by placing a nickel in contact with the coated substrate at about a 45-degree angle so that the sharp edge of the nickel was in contact with the coating surface. The nickel was then pulled toward the operator at a moderate rate and with moderate to heavy pressure. The scraped coating area was observed for delamination/whitening, surface mar and/or coating removal, *i.e.* topcoating removal from undercoating or removal of the entire coating system from the substrate.

#### **Tape adhesion test (ASTM D3359)**

The tape adhesion test was conducted according to the specification of ASTM D3359, which is hereby incorporated by reference. The test was conducted by making 2 sets of 6 parallel cuts (spaced 2mm apart), at right angles to one another, into the coated substrate with sufficient pressure to just go through the coating to the substrate. A cutting tool kit purchased from Paul N. Gardner Co. of Pompano Beach, FL was used. After making the crosshatched cuts into the coated substrate, the cut area was brushed clean of loose coating debris and 1-inch width Permacel tape was pressed onto the crosshatched area and pressure applied with a plastic bar in order to assure intimate contact of the tape with the cut area. The tape was then removed from the surface at about a 90-degree angle with a medium but uniform motion. The area was observed for removal of coating from the substrate and/or release of topcoating layers from interior coating layers. Results were reported as follows:

- 5B no (0%) area removed
- 4B less than 5% area removed

- 3B 5 - 15% area removed
- 2B 15 - 35% area removed
- 1B 35 - 65% area removed
- 0B greater than 65% area removed

The tested area was compared to pictorial depictions given in the ASTM D3359 standard for results. Results may also be described on a scale from "Excellent", "Very Good", "Good", "Poor" to "Very poor".

## Examples

### **Example 1:**

The quality of the Formulation C stains were tested by applying the stains to red oak veneer that had been scuff sanded with 220 stearated paper. Formulation C, batch (i) and batch (ii) were applied at 21°C and 48% relative humidity. The Formulation C stain was compared to Formulation E (aged) stain.

All the stains wiped the same, and had similar appearance. Next, the stained veneer was cured for 10 minutes at 200°F, and cooled for 5 minutes. Next, a UV-curable coating based on a polyester acrylate/urethane acrylate blend was applied with a 5 RDS rod. The UV-clear coating was cured by passing through an American ultraviolet UV conveyor in one pass at 14 ft/minute using a 300 Watt lamp. The cure energy that the product was exposed to was 887mj/cm<sup>2</sup>, UVA. The coated veneer was sponge sanded with a fine sanding sponge from 3M company. Next, the UV coating was applied a second time, and the substrate was again cured as described above.

Tape adhesion appears excellent on all three sample areas, and nickel adhesion appears very good on all three.

### **Example 2:**

Formulation C was run on a production-type sponge roller machine with 2 brushes following. The stain applied well. The stain brushed out well. The stain was run on red oak veneer and solids. Two grades of veneer were utilized, *i.e.* good veneer and poor veneer; the good veneer was of much higher quality than the poor veneer. All parts were scuffed with 220 stearated prior to staining. The stained parts were run through an oven twice at some temperature. It was estimated that the board surface temperature out of the oven the second time was about 130°F.

The grain raising results for the good veneer and the poor veneer are summarized as follows:

**Good veneer**

1. Flake Results  
—Good result; minimum grain raise; better than typical water based stain.
2. Open grain Results  
—Grain raising about equal to typical water-based stain

**Poor veneer**

1. Flake Results  
—Good result; grain raising reported to definitely be better than typical water based stain. This wood is particularly troublesome as typical water-based stains cause severe splitting over this "ruddy or shoddy" wood.
2. Open grain Results  
—Grain raising about equal to typical water-based stains

**Solids**

- Grain raising about equal to typical water-based stains

The overall grain raising results of the Formulation C stain were somewhat encouraging, but not outstanding.

Because water-based stains have to be run at substantially higher solids than solvent based stains in order to obtain good adhesion and improve grain raising, build-up on the brushes is a problem. It is expected that Formulation C stain will not build up significantly on the brushes because it is only about 10% solids, and its vehicle solids is only about 2.5%. Thus from the standpoint that Formulation C is only about 1/3 the level of solids as a typical acrylic based aqueous stain, it is expected that there will be reduced build-up on the brushes.

It was viewed that grain raising directly in the pore was better than having grain raising on the flake because these fibers may be knocked off with brushlon denibber sanding. The potential advantage of this formulation compared to more typical water based stains includes less grain raising and reduced stain build-up on brushes.

When some of these parts were sanded with a scotch-brite™ pad (commercially available from 3M, St. Paul, MN), the area directly adjacent to the open grain, (the "latewood-earlywood interface"), had some of the stain color removed, particularly when scotch-briting heavily. This "reverse shadow effect" is common to typical water-based stains, but was minimal for this stain. (Subsequent

coating with sealer did not show a large effect here which is a definite positive result). The "reverse shadow effect" is somewhat common to water based stains when they are run through the brushlon denibbers under a lot of pressure or are denibbed very aggressively. This is usually done in order to minimize the effects of grain raising somewhat. However, this usually translates into the need for substantial amounts of tinting on line and attempts to control color with the denibbing brushes. It appears that less scotch-briting may be required with Formulation C stain because the flake seemed smoother than with conventional water-based stains.

After coating parts with sealer, the brightness of the stained parts and color contrast was very good, which is an advantage because dark colored aqueous stains can be muddy in appearance with low contrast. The sealer was applied and cured incompletely two times, and then applied a third time and fully cured. (There was no sanding in between the applications of the sealer.) The adhesion results are given in Table 11.

*Table 11. Adhesion Results of UV Sealer Over Formulation C (CMCAB-Based Stain)*

Panel Designation of Coating Manufacturer	Red Oak Wood Type	Tape crosshatch adhesion (ASTM D3359 test)	Nickel adhesion
Panel 1	Oak veneer – poorer quality	4B	Good
Panel 2	Oak veneer – poorer quality	5B	Very good – excellent
Panel 3	Oak veneer – poorer quality	4B	Very good – excellent
Panel 4	Oak veneer – poorer quality	2B-3B	Very good – excellent
Panel 5	Oak veneer – higher quality	5B	Very good
Panel 6	Oak veneer – higher quality	4B	Good
Panel 7	Oak veneer – higher quality	4B	Good
Panel 8	Solid oak	1B	Fair
Panel 9	Solid oak	1B	Fair – slight good
Panel 10	Solid oak	3B	fair

The ASTM D3359 test was performed according to the protocol of the American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103. These results indicate that the adhesion on the veneered panels appears acceptable; however, the adhesion on the solid oak panels is not acceptable.

Adhesion to solid red oak is typically problematical. Where adhesion was not lost, it appeared that the stain was pulled apart somewhat.

The grain raising of the solid oak and the highest quality veneer was satisfactory; however, the grain raising of the poor quality veneer was unsatisfactory. However, it is noted that the poor quality veneer would typically be filled with UV filler.

***Example 3:***

The effect of various commercial pigment dispersions on CMCAB-based stain adhesion was evaluated. The goal here was to develop stains at approximately a 2/1 P/B.

The stains were applied to red oak veneer with a rag. Formulation J was used as the control. The stained panels were dried at 120°F for 19 minutes and cooled for 10 minutes. A UV topcoat was applied by 5 RDS draw down. The UV-clear coating was cured by passing through an American ultraviolet UV conveyor in one pass at 10 ft/minute using a 300 Watt lamp. The cure energy that the product was exposed to was 1206mj/cm<sup>2</sup>, UVA. The first coat was sponge sanded and a second coat applied and cured in the same manner. The following table summarizes stain application and adhesion results.

*Table 11. Effect of Commercial Pigment Dispersions on Application and Adhesion of CMCAB-Based Aqueous Stains*

Sample	Wiping Vs Control	Tape Adhesion		Nickel Adhesion	
Formulation		Control	Sample	Control	Sample
K	Wipes good. low color development	Excellent	Excellent	V. good	V. good
L	Good	Excellent	Excellent	V. good	V. good
M	Good. v. low color development	Excellent	Excellent	Approx. excellent	Approx. excellent
N	Good. v. low color development	Excellent	Excellent	V. good	excellent
O	Good./ v. low color development	Excellent	Excellent	V. good	V. good
P	Good-color sl. More bright after coating	Excellent	Excellent	Approx. excellent	Approx. excellent
Q	Good; low color development	Excellent	Excellent	V. good	V. good

The adhesion of all stains, made with the various pigment dispersions, look good. The wiping of all stains appears good. From this standpoint, this CMCAB formula appears fairly robust under this UV system. From a white stain standpoint,

none of the stains appear to be white enough. Formulation K, Sunperse white WHD 9507, appears to produce the most whiteness, then Formulation Q, Daniels/Elementis white CW5003, the next most white. This may indicate the need to increase the amount of TiO<sub>2</sub> fairly dramatically.

Although the invention has been described in some detail by way of illustration for purposes of clarity of understanding, it will be apparent to those of ordinary skill in the art that various modifications and equivalents can be made without departing from the spirit and scope of the invention. It should be understood that the foregoing discussion and examples merely present a detailed description of certain preferred embodiments. All the patents, journal articles and other documents discussed or cited above are herein incorporated by reference in their entirety.

The claimed invention is:

1. A method for making a stained wood substrate having an overcoat with improved adhesion of the overcoat, comprising the steps of:
  - applying an aqueous carboxymethyl cellulose acetate butyrate stain composition to a wood substrate,
  - drying the stained wood substrate,
  - applying an overcoat to the stained wood substrate, and
  - curing the coated, stained wood substrate,

wherein the aqueous carboxymethyl cellulose acetate butyrate stain composition comprises

  - carboxymethyl cellulose acetate butyrate;
  - optionally, a colorant;
  - water; and
  - an organic solvent.
2. A method of claim 1, wherein said wood substrate comprises at least one type of wood selected from the group consisting of: oak, maple, yellow pine, birch, spruce, walnut, poplar, cherry, and aspen.
3. A method of claim 1, wherein the carboxymethyl cellulose acetate butyrate has a degree of substitution of carboxymethyl of 0.20 to 0.75, a degree of substitution per anhydroglucose unit of hydroxyl from about 0.10 to 0.70, and a degree of substitution per anhydroglucose unit of butyryl of about 0.10 to 2.60 and a degree of substitution per anhydroglucose unit of acetyl of 0.10 to 1.65.
4. A method of claim 3, wherein the carboxymethyl cellulose acetate butyrate has a degree of substitution per anhydroglucose unit of hydroxyl from about 0.10 to 0.70, butyryl from about 1.10 to 2.55, and acetyl from about 0.10 to 0.90.
5. A method of claim 4, wherein the carboxymethyl cellulose acetate butyrate has an inherent viscosity of 0.20 to 0.70 dL/g, as measured in a 60/40 (wt/wt) solution of phenol/tetrachloroethane at 25°C.
6. A method of claim 1, wherein the colorant is selected from the group consisting of titanium dioxide, zinc oxide, zinc sulfide, white lead, lithophone, mineral blacks, bone blacks, iron oxide blacks, carbon blacks, lead chromates, metal oxides, sulfides, sulfoselenides, iron blue, cobalt blue, ultramarine blue, manganese violet, bismuth vanadate, molybdate yellow, lithol reds, permanent red 2B, lithol rubine red, BON reds, BON maroon-nonmetallized azo reds, toluidine red, para reds, naphthol reds, quinacridone reds, vat reds, anthraquinone red, brominated pyranthrone red, perylene reds, benzimidazolon based reds, diazo condensation reds, thioindigoid reds, pigment red 251, 252, and 257, copper phthalocyanine blues, indanthrone blue, carbazole violet, monoarylide

yellows, diarylide yellows, benzimidazolone yellows, heterocyclic yellows, azo-based oranges, bisazo-based oranges, bisazo condensation-based oranges, perinone type orange, quinacridone type orange, pyranthrone type orange, heterocyclic hydroxy-based orange, pyrazoloquinazolone-based orange, copper phthalocyanine greens, triphenylmethane-phospho tungsto molybdic acid (PTMA) complexes, calcium carbonate, kaolin or china clay, talc, silica, mica, barium sulfate, wollastonite, sodium aluminosilicates, alumina trihydrate, aluminum oxide, aluminum, zinc, gold, bronze, nickel, stainless steel, titanium dioxide, ferric oxide coatings on mica, bismuth oxychloride crystals grown from a solution of bismuth salts, natural pearl essence, guanine, hypoxanthane purines from fish scales, acid dyes, azoic coupling components, azoic diazoic components, basic dyes, direct dyes, reactive dyes, solubilized vat dyes, solvent dyes, sulfur dyes, vat dyes, aniline dyes, and mixtures thereof.

7. A method of claim 1, wherein the wood stain formulation further comprises one or more coatings additives selected from the group consisting of plasticizers, waxes, organic bases, inorganic bases, leveling agents, flow control agents and rheology modifiers; flattening agents; pigment wetting and dispersing agents; surfactants; ultraviolet (UV) absorbers; UV light stabilizers; tinting pigments; defoaming and antifoaming agents; anti-settling, anti-sag and bodying agents; anti-skimming agents; anti-flooding and anti-floating agents; fungicides and mildewcides; corrosion inhibitors; thickening agents; coalescing agents; and mixtures thereof.
8. A method of claim 7, wherein the wood stain formulation further comprises a plasticizer as an additive.
9. A method of claim 8, wherein the plasticizer is selected from the group consisting of texanol isobutyrate, diisononyl phthalate, dioctyl phthalate, butyl benzyl phthalate, dibutyl phthalate, diethylene glycol, dioctyl terephthalate, and mixtures thereof.
10. A method of claim 1, wherein the wood stain formulation comprises an organic solvent selected from the group consisting of acetone, methyl ethyl ketone, methyl isobutyl ketone, methyl amyl ketone, methyl isoamyl ketone, 2-propoxyethanol, 2-butoxyethanol, ethyl 3-ethoxypropionate, 2-butanone, methanol, ethanol, propanol, isopropyl alcohol, butanol, 2-ethyl-hexanol, ethyl acetate, propyl acetate, isopropyl acetate, butyl acetate, isobutyl acetate, ethyl ether, propyl ether, propyl glycol butyl ether, diethylene glycol methyl ether, diethylene glycol ethyl ether, diethylene glycol butyl ether, dipropylene glycol ether, dipropylene glycol methyl ether, ethylene glycol, ethylene glycol butyl ether, ethylene glycol diethyl ether, ethylene glycol dimethyl ether, ethylene glycol ethyl ether, ethylene glycol 2-ethylhexyl ether, ethylene glycol methyl ether, ethylene glycol phenyl ether, 1-methyl-2-pyrrolidinone, ethylene glycol diacetate, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether, ethylene glycol monobutyl ether, ethyl ether, propylene glycol butyl ether, propylene glycol dimethyl ether, propylene glycol ethyl ether acetate, propylene glycol methyl ether, propylene glycol ethyl ether, propylene glycol propyl ether, propylene glycol butyl ether, propylene glycol methyl ether acetate, propylene

glycol phenyl ether, propylene glycol propyl ether, propylene glycol, tripropylene ethyl ether, triethylene glycol, tri(ethylene glycol) dimethyl ether, and mixtures thereof.

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